VI. *Some Experiments and Observations on a new Substance which becomes a violet coloured Gas by Heat.* *By Sir* Humphry Davy, *Knt. LL. D. F. R. S.*

Read January 20, 1814.

A NEW and a very curious substance has recently occupied the attention of chemists at Paris.

This substance was accidentally discovered about two years ago by M. COURTOIS, a manufacturer of saltpetre at Paris. In his processes for procuring soda from the ashes of sea weeds, (cendres de vareck) he found the metallic vessels much corroded; and in searching for the cause of this effect, he made the discovery. The substance is procured from the ashes, after the extraction of the carbonate of soda, with great facility, and merely by the action of sulphuric acid:—when the acid is concentrated, so as to produce much heat, the substance appears as a vapour of a beautiful violet colour, which condenses in crystals having the colour and the lustre of plumbago.

M. COURTOIS soon after he had discovered it, gave specimens of it to M. M. DESORMES and CLEMENT for chemical examination; and those gentlemen read a short memoir upon it, at a meeting of the Imperial Institute of France, on Nov. 29th. In this memoir, these able chemists have described its principal properties; they mentioned that its specific gravity was about four times that of water, that it becomes a violet coloured gas at a temperature below that of boiling water, that it combines

with the metals and with phosphorus and sulphur, and likewise with the alkalies and metallic oxides, that it forms a detonating compound with ammonia, that it is soluble in alcohol, and still more soluble in ether; and that by its action upon phosphorus and upon hydrogen, a substance having the characters of muriatic acid is formed. In this communication they offered no decided opinion respecting its nature.

M. AMPERE had the goodness to give me some of this substance, and M. CLEMENT having requested me to submit it to some analytical tests, I made several experiments upon it, which convinced me that it was a new substance undecompounded in any of the circumstances to which I was able to expose it; and that the acid formed in processes upon it was not muriatic acid, but a new acid possessing a striking resemblance to that body.

M. GAY LUSSAC (to whom M. CLEMENT had furnished some of the substance, and with whom he had made some experiments upon it before the communication of his memoir) on Monday, Dec. 6, read to the Institute a paper, in which he stated that the acid formed by its action on hydrogen is a peculiar one. He mentioned several interesting particulars respecting the mode of its production, and he compared it to oxymuriatic gas or chlorine, and stated that two hypotheses might be formed on its nature; and that it might be considered as an undecompounded substance, or as a compound of oxygen; M. GAY LUSSAC is still engaged in experiments on this subject, and from his activity and great sagacity, a complete chemical history of it may be anticipated. But as the mode of procuring the substance is now known to the chemical world in general, and as the combinations and agencies of it offer an

extensive field for enquiry, and will probably occupy the attention of many persons, and as the investigation of it is not pursued by the discoverer himself, nor particularly by the gentlemen to whom it was first communicated, I shall not hesitate to lay before the Royal Society an account of the investigations I have made upon it; and I do this with the less scruple, as my particular manner of viewing the phenomena has led me to some new results, which probably will not be considered by the Society as without interest in their relation to the general theory of chemistry, and in their possible application to some of the useful arts.

The first experiments that I made on this substance, were to ascertain whether (argentane) muriate of silver could be formed from its solution in water or alcohol, and for this purpose it was purified by distilling it from lime. Its solution I found, when mixed with solution of nitrate of silver, deposited a dense precipitate of a pale lemon colour; this precipitate when collected and examined, proved to be fusible at a low red heat, and then became of a red colour. When acted upon by fused hydrate of potassa, it was rapidly decomposed, and a solid substance, having all the characters of oxide of silver, was formed. The matter soluble in water separated by a filter, and, acted upon by sulphuric acid, afforded the peculiar substance.

A solution of potassa, after being boiled on the precipitate, afforded the peculiar substance, when treated by the same acid.

The precipitate was much more rapidly altered by exposure to light, than the muriate of silver, and was evidently quite a distinct body.

Conceiving from the action of potassa upon it, that it must be a compound of the peculiar substance and silver, I endeavoured to form it directly by the combination of the two bodies. I introduced some of the substance into the closed end of a small glass curved tube, and placed in the upper part of it some silver foil; I heated the foil nearly to redness, and then passed the substance over it in vapour; there was an immediate action, the silver was rapidly dissolved, and a fusible substance formed, in all its obvious sensible and chemical characters, the same as that obtained from solutions of the substance by nitrate of silver.

The modes which occurred to me, as most likely to effect its decomposition by chemical agents, were the action of the highly inflammable metals upon it which unite to oxygen and chlorine, or the action of chlorine which in general tends to the expulsion of oxygen, and to the separation of inflammable bases from that principle.

I heated some potassium in a little glass tube, and passed some of the substance in vapour over it; at the moment the vapour came in contact with the potassium, there was an inflammation, and the potassium burnt slowly with a pale blue light. There was no gas disengaged when the experiment was repeated in a mercurial apparatus.

The substance formed by the action of potassium was white, fusible at a red heat, and soluble in water. It had a peculiar acrid taste. When acted upon by sulphuric acid, it effervesced, and the peculiar substance appeared.

It was evident that in this experiment there had been no decomposition of the body; the result seemed to depend merely upon the combination of it with the potassium.

I exposed the body to the action of chlorine in a small glass tube; it absorbed the chlorine, and a substance formed which was volatile by heat, and which appeared as a yellow solid; it was soluble in water, and rendered the water of a yellowish green colour and strongly acid, the solution when acted upon by solution of potassa not in excess effervesced, and afforded the peculiar substance.

The acid formed by the solution of the substance united to chlorine reddened vegetable blues by its immediate contact, and soon after destroyed them.

When the new substance was heated in oxygen gas, or brought in contact with red hot hyperoxymuriate of potassa, it seemed to undergo no change.

M. M. DESORMES and CLEMENT had stated, that, when the substance is combined with the metals, metallic oxides could be obtained from the solutions; I suspected that this depended upon the presence of moisture, or upon oxygen derived from the air, and experiment justified my suspicion.

I heated the substance with iron, mercury, tin, zinc, and lead, out of the contact of air; it united to them without any violence of action, and formed compounds fusible at a moderate heat, and volatile at a higher temperature. All the compounds, except that of zinc, which was white, were coloured of different shades of red brown, red and orange; the compound it formed with tin was of a deep orange, that with iron of a bright red brown, that with lead a bright orange, that with mercury an orange still more approaching to red, and which, when crystallized, was bright crimson.

The compound of iron and the substance, when exposed to an alkaline solution, immediately deposited black oxide of iron;

but when I heated it in a small retort, containing pure ammoniacal gas, no such change occurred, and it combined with the ammonia and formed a compound which volatilized without leaving any oxide.

The compound of the substance with tin was soluble in water, and had the characters of an acid. It combined with the alkalies without depositing oxide.

The crimson compound of the substance with mercury united in the same manner without decomposition to potassa, and by the action of sulphuric acid, sulphate of potassa was formed, and the compound of the substance with mercury disengaged.

When the substance is made to act upon phosphorus, the two bodies combine with great rapidity at common temperatures, producing heat without light; small quantities of a strongly acid gas generally arise from the mixture, and by the application of heat, it is produced in greater quantities. When the substance is in excess, an easily fusible and volatile compound of a red colour is obtained; when the phosphorus is in excess, the greater part of the product is more fixed.

I examined the gaseous acid formed by the action of phosphorus with attention. It gives dense white fumes by combining with the aqueous vapour in the air. It has a smell very similar to that of the solid compound of chlorine and phosphorus, which itself is very analogous to that of muriatic acid. It is rapidly absorbed by water. When made to act upon ammonia, it forms with it a dense white salt, which, when acted upon by sulphuric acid, affords the peculiar substance, and at the same time a smell of hydrogen is perceived. When mercury is heated in the acid gas, the same compound as that

produced by the action of the new substance directly upon mercury is formed, and hydrogen equal to half the volume of the gas is disengaged. When potassium is made to act upon it, there is no inflammation as in muriatic acid gas, but the potassium becomes converted into a body, similar to that produced by its combustion in the vapour of the substance, and a gas equal to half the volume of the acid gas, which burns in the same manner as hydrogen, is disengaged.

When the easily fusible and volatile compound of the substance with phosphorus is heated in water, it rapidly dissolves in it, and forms a strong acid, which, when evaporated, leaves hydrophosphorous acid, and which, before its evaporation, neutralized by potash, and acted on by sulphuric acid, affords the peculiar substance.

When the difficultly fusible substance it forms with phosphorus is acted on by a small quantity of water, and heated in a glass tube, much gas spontaneously inflammable is disengaged, and a white sublimate arises, which, when acted on by cold water, becomes hot, and affords a considerable quantity of a gas having all the properties of hydrophosphoric gas.

The solution of this crystalline substance in water, neutralized by potash, and decomposed by sulphuric acid, afforded the peculiar substance, but when the solution was heated strongly before its neutralization, it left only hydrophosphorous acid, which when heated gave off hydrophosphoric gas, and became phosphoric acid.

It is easy to explain all these phenomena, except the production of the acid gas, which is a compound of the peculiar substance and hydrogen: to account for the appearance of

this body, it is necessary to suppose the existence of hydrogen, or of water in the substance, or of hydrogen in phosphorus.

I used the substance distilled through quick lime, which there is every reason to believe would absorb all the water united to it: in this case the acid gas, which gave hydrogen when decomposed by mercury, was produced in much smaller quantities; but, when the substance was moistened, the gas was afforded in very large quantities. It is probable, that a little hydrogen existing in the phosphorus, and which appears when that substance is acted on by Voltaic electricity, may influence the result; but I am inclined to attribute it principally to the moisture adhering to the substance, and I have never been able to produce more gas from the fusible compound by distilling it with a new quantity of phosphorus.

When the fusible compound of the substance with phosphorus is distilled with a small quantity of water, the gas produced seems to be of the same kind as that obtained by the action of heat during the combination, and both these gases when absorbed by water afford, when acted upon by nitrate of silver, the same product as that formed by the action of a solution of the substance in water on the same salt.

I attempted to form a compound of the substance with hydrogen directly, by heating it in several experiments to redness in a glass tube filled with hydrogen. When the gas was moist, or when the tube contained vapour, a strong acid fluid was formed of a deep yellow colour. When the gas and the substance were dry, there was an expansion of volume, and on breaking the tube, fumes appeared similar to those produced by the action of the gas formed during the union of phosphorus and the substance, and which precipitated in the

same manner a solution of nitrate of silver. This peculiar acid, which consists of the substance united to hydrogen, has a very strong attraction for water, and a very small quantity of water absorbs a large quantity of the gas, and when combined with water, it rises with it in vapour, and in its state of liquid acid, it rapidly dissolves the substance, and becomes tawny.

The new substance, as M. M. DESORMES and CLEMENT have shewn, is rapidly soluble in solution of potash; when it is in excess the solution becomes red brown. On evaporating the mixture and heating it to redness, a substance is formed, exactly similar to that produced by the combination of the substance with potassium.

As potassa is a compound of potassium and oxygen, it is evident that, to form a compound of potassium and the substance from potassa, oxygen must be expelled, and I found by experiment, that this was the case; and in investigating minutely the action of fixed alkaline solutions on the substance, I ascertained the existence of a class of substances, precisely similar to the hyperoxymuriates, consisting of oxygen, the substance, and potassium, and formed in a manner exactly analogous.

If the substance is thrown into a moderately strong solution of potassa as it dissolves, crystals fall down, and by saturating the solution with the substance, considerable quantities are obtained. By pouring off the mother liquor and evaporating it a little, more of the crystals fall down.

All these crystals, if precipitated from a solution not too much saturated, are of the same kind, they are little soluble in water, have a taste analogous to that of the hyperoxymu-

riates of potassa, scintillate when thrown upon burning coals, and form a deflagrating mixture when mixed with charcoal. When fused, they give off abundance of oxygen gas, and become the same substance as that formed by the action of potassium on the new substance.

If the liquor which has ceased to afford the crystals be evaporated to dryness, it yields a considerable quantity of a substance which is not capable of detonating with combustible bodies, and which is the same as that afforded by the combination of the substance with potassium.

It is evident then that the oxygen contained in the potassa is newly combined by the action of the new substance, and two compounds formed, one consisting of potassium and the new substance, the other of potassium, the new substance, and the oxygen contained in the potassa.

By passing the vapour of the substance over dry red hot potassa formed from potassium, oxygen is expelled, and it appears that oxygen cannot remain in the triple compound at a heat above the red heat.

By dissolving the substance in solutions of soda and baryta similar results are obtained, and in each case two compounds are formed. The oxygen is condensed in one, and the other consists simply of the new substance and a metal.

To separate entirely the deflagrating salt from the soluble salt is not easy, there always remains in the mother liquor a little of the deflagrating compound; but by separating the first crystals from solution of potassa not too strong, the deflagrating compound of oxygen, potassium, and the substance is obtained, apparently pure.

As the new substance combines with potassium and the

metals with much less energy than chlorine, it occurred to me, that it would probably be expelled from its combinations by that body; and this I have found to be the case in all the experiments I have made. When the compound of the new substance and potassium is heated in contact with chlorine, potassane (muriate of potassa) is formed, the violet gas appears, but soon combines with chlorine, and they form together the peculiar acid compound I have before described; but towards the end of the process, as the proportion of chlorine diminishes, the violet coloured gas again appears.

When the compound of the substance with silver was treated in the same manner (argentane) muriate of silver was formed, and the substance combined with chlorine at the commencement of the operation, but was disengaged uncombined towards the end.

Similar phenomena occurred when the compounds of the substance with mercury and lead were acted on by chlorine.

The action of acids on the compounds of this substance, are what might be expected from its analogies to chlorine.

When concentrated sulphuric acid is poured upon the compound of the substance and potassium, some of the substance appears; but a part of it rises in combination with hydrogen and water, and condenses by cold, and appears of a deep orange colour from having dissolved some of the substance. The sulphuric acid likewise seems to retain some of the substance, for it continues red after being strongly heated, and the acid is partly decomposed, for sulphurous acid gas is disengaged.

It seems probable, that the acid is decomposed to furnish oxygen to a portion of the potassium which quits in consequence the new substance, and that water is likewise decomposed to

furnish hydrogen to another portion of the substance, and that the hydrogen and the substance, in their acid form, combine with the water of the sulphuric acid, and rise in vapour, sulphate of potassa being at the same time produced.

When sulphuric acid is poured on the salt consisting of the substance, oxygen, and potassium, the substance reappears, and there is a slight effervescence. In this case, part of the oxygen is employed to form potassa, and the remainder is expelled unaltered.

When concentrated nitric acid is made to act on the triple compound, similar phenomena occur, and the substance reappears with effervescence.

When nitric acid is applied to the double compound, there is a smell of nitrous gas, and the substance is instantly reproduced.

With concentrated muriatic acid, the phenomena presented by the two different alkaline compounds, the binary and the triple, are very interesting. When the acid is brought in contact with the triple salt, there is no effervescence, but a substance, which appears to be a compound of chlorine and the new body, is formed and dissolved in the water of the acid, and potassane is precipitated.

When the double compound is used, there is a complete solution with a partial decomposition, and by applying a gentle heat, the excess of muriatic acid is driven off, and the same acid as that procured by the action of the substance on hydrogen remains dissolved in the liquor. When mixtures of the two salts are employed, the substance itself appears.

It appears that in the instance when the triple compound is employed, there is not only sufficient oxygen to attract the hydrogen from the chlorine which is to combine with the

potassium, but likewise enough to decompose a portion of muriatic acid, sufficient to afford chlorine to enter into combination with the whole of the substance.

When the binary compound is used, the result is a simple instance of double affinity; the new substance quits the potassium to unite to the hydrogen of the muriatic acid, and the chlorine and the potassium combine: and that the decomposition is only partial depends probably upon the attraction of the compound of iodine and potassium for water. When mixtures of the compounds are used, the oxygen is employed to attract hydrogen from the substance, to which it seems to adhere with a much weaker attraction than to chlorine.

M. M. DESORMES and CLEMENT have mentioned, that when the new substance is exposed to liquid ammonia, a black powder is formed, which, when dry, fulminates by the slightest contact or friction. I introduced some of the substance into solution of ammonia, and separated the liquor from the black powder, and evaporated it to dryness; it left a white saline substance, the same as that produced by the union of ammonia with the peculiar acid, which consists of the substance combined with hydrogen; and hence it appeared probable that a portion of ammonia had been decomposed to furnish hydrogen.

I made the experiment on the action of strong solution of ammonia on the substance in a pneumatic apparatus; but no azote was given off. Hence I am induced to conclude, that the black powder is a compound of the new substance and azote, similar in its character of a binary compound to the detonating oil discovered by M. DULONG; and this conclusion is strengthened by the results of its detonation in a tube of glass partially exhausted: they are, I find, the peculiar

substance and a gas which is not inflammable, and which does not support flame; and unless the substance is moist, I have never been able to discover any other product; but the minute quantity I have employed prevents me from being confident on this point.

It was an object of considerable interest to ascertain the proportion in which the new substance combines, as compared with that in which the other substances that form acids by their action on inflammable bodies enter into union.

I made several experiments on this subject. 4 grains of hydrate of potassa, I found, were saturated by 6.25 of the new substance, and 2.8 the quantity of potassium in 4 grains of hydrate of potassa is to 6.25 the quantity of the substance, as 75, the number representing potassium, is to 166. Again, 1 grain of hydrate of soda required 2.1 grains of the new substance for its saturation, and 1 grain of hydrate of soda contains .578 of sodium, so that supposing the combination of the new substance with sodium to contain a double proportion of the substance, the number representing the proportion in which it combines will be nearly 160.

Two grains of the compound of the substance with sodium decomposed by sulphuric acid afforded 128 of dry sulphate of soda, and calculating on this experiment the number is 165.5.

I have made some experiments on the quantity of the substance absorbed by tin, mercury, and lead. Mercury absorbs nearly $\frac{3}{4}$ of its weight of the new body to become the crimson substance; from which it appears that it must absorb two proportions.

My experiments have been made upon quantities too small to afford very exact results; but they shew that the new

substance enters into union in a quantity much more than twice as great as that of chlorine, and, considered as an element, it offers a number much higher than those of the simple inflammable bodies, and higher even than those of most of the metals.

The most correct mode of ascertaining the number representing the proportion (supposing it to be definite, as is the case with all other bodies that have been accurately examined) in which it combines, will probably be by ascertaining the specific gravity of its gaseous compound with hydrogen. This gas, as I have stated, affords only half its volume of hydrogen, and it appeared to me to neutralize an equal volume of ammonia, so that supposing it to consist of two proportions of hydrogen, and only one of the substance, that is, to be analogous to muriatic acid gas in its nature, it must be one of the heaviest elastic fluids existing.

Taking the number representing the proportion in which the new substance combines as 165, and supposing that it occupies the same volume in this gas that chlorine occupies in muriatic acid gas, 100 cubical inches of the gas will weigh at mean temperature and pressure 95.27 grains, *i. e.* supposing hydrogen in the same quantity to weigh 2.27 grains.

I am not at present in possession of an apparatus for weighing the gas with accuracy. A particular device will be required for this purpose, as the gas cannot be preserved over mercury. It may be collected during the action of phosphorus on the moistened substance in a vessel exhausted of air; or it may be made by heating the compound of the substance and potassium in muriatic acid gas in a glass vessel: in this case, there is, I find, a double decomposition, the chlorine quits the

hydrogen to unite to the potassium, and the substance quits the potassium to unite to the hydrogen.

The new substance, I find, is not decomposed when Voltaic sparks are taken in it in its gaseous state from ignited points of charcoal: at first there are white fumes, probably from the action of moisture or hydrogen in charcoal, on the substance; but these fumes soon cease, and when the tube in which the experiment is made is cooled, the substance appears unaltered.

From all the facts that have been stated, there is every reason to consider this new substance as *an undecompounded body*. In its specific gravity, lustre, the high number in which it enters into combination and colour, it resembles the metals; but in all its chemical agencies it is more analogous to oxygen and chlorine; it is a non-conductor of electricity, and possesses, like these bodies, the negative electrical energy with respect to metals, inflammable and alkaline substances, and hence when combined with these substances in aqueous solution and electrized in the Voltaic circuit, it separates at the positive surface; but it has a positive energy with respect to chlorine, for when united to chlorine in the compound acid I have described, (page 78), it separates from the chlorine at the negative surface. This likewise corresponds with their relative attractive energy. Chlorine expels the new substance from all its combinations on which I have made any experiments.

The new substance seems to possess a stronger attraction for most of the metals than oxygen; but it is expelled from phosphorus and sulphur by oxygen: I found by passing oxygen and the compound of it with phosphorus through a glass tube heated red, phosphorous acid was formed, and the violet gas appeared.

That it produces so little heat and so seldom light in entering into combination, may be accounted for from its solid form and its great weight as an element. Potassium, however, as I have mentioned, burns in the violet coloured gas, and when this gas is thrown upon the flame of hydrogen, it seems to support its combustion.

The saturating or neutralising powers of the new substance appear to be greater than those of oxygen, and less than those of chlorine.

It agrees with chlorine and fluorine in forming acids with hydrogen, and it agrees with oxygen in forming an acid with chlorine.

In my first experiments I conceived that it formed substances analogous to alkalies in combining with the alkaline metals, for the compound produced by its action upon solution of potassa, even when the substance was in great excess, reddened turmeric paper, and rendered green paper tinged with the juice of violets; but I have since found that this is owing to a small quantity of subcarbonate of potassa which existed in the hydrate of potassa; and when the compound is treated with the acid the substance forms with hydrogen, and heated to redness, it loses this property; and when thus formed, its taste more resembles that of a neutral salt than of an alkali. I cannot yet say with certainty whether its compound with potassium has powers like the oxides, of neutralising those acids which it does not decompose, as in all the experiments I have made on this point I used the compound which reddens turmeric; this neutralised the phosphorous, sulphurous, and boracic acids, but the effect may possibly depend upon the undecomposed carbonate.

The name *ione* has been proposed in France for this new substance from its colour in the gaseous state, from ἴον, viola; and its combination with hydrogen has been named *hydroionic acid.* The name *ione*, in English, would lead to confusion, for its compounds would be called *ionic* and *ionian.* By terming it *iodine*, from ἰώδης, violaceous, this confusion will be avoided, and the name will be more analogous to chlorine and fluorine.

The acid it forms with hydrogen may, however, be with propriety named in our language *hydroionic acid.* I venture to propose for the acid it forms with chlorine, the name of *chlorionic acid*, and for that it forms with tin *stannionic acid.* With respect to the other compounds, they may be called as a class *iodes*, with the name of the base as *iode of mercury*, and with *proto*, *deuto*, &c. to signify the proportions; or if a termination to the base should be preferred, as I have proposed for the combinations of chlorine, the terminations may be in *m*, with the vowels in their usual order to signify proportions. Thus, phosphoroma would signify the combination of one proportion of iodine with phosphorus, and phosphoromè would signify two proportions of iodine to one of phosphorus.

If this last plan, which involves no theoretical views, should be adopted, it may be extended with different consonants to the combinations of *fluorine*, and the vowel may be made to signify the proportion, and the consonant the nature of the compound. The vowel of termination, to the Latin name of the base, I have already proposed, on another occasion, for the compounds of oxygen. Thus argenta may be made to signify the protoxide of silver, and ferrè the deutoxide of iron. *n* is the consonant which I have suggested to

represent the combination of chlorine, as *argentana* the *protochloride* of silver; and *l* in this system may represent fluorine. Thus *calcala* would be fluor spar, or one proportion of fluorine, and one of calcium, and the different combinations of calcium with the supporters of combustion with oxygen, fluorine, chlorine, and iodine in one proportion, would be thus expressed *calca*, *calcala*, *calcana*, and *calcama*.

I throw out these hints for discussion, rather than with any wish for their adoption, and for the purpose of directing the attention of chemists towards the subject of nomenclature, which ought to be settled on some fixed principles; and in naming a new class of compounds, great caution should be used to prevent the necessity of alteration.

In my last paper, presented to the Society two months ago, I ventured to suggest that it was probable, that new species of matter, which act with respect to inflammable bodies, like oxygen, chlorine, and fluorine, would be discovered. I had not hoped, at that time, to be able so soon to describe the properties of a body of this kind, which forms an acid with hydrogen, like chlorine and fluorine, and which in some of its combinations resembles oxygen.

This new fact will, I hope, do something towards settling the opinion of chemists respecting the nature of acidity, which seems to depend upon peculiar combinations of matter, and not on any peculiar elementary principle.

It is probable that *iodine* will be found in many combinations in nature. We may expect that it will be discovered in various marine vegetables, and in sea water, and probably the loss of weight indicated in the analysis of certain fossil substances may depend upon its expulsion.

Its compounds with the metals will probably form a new class of pigments, and it is not impossible, that the triple salts it forms containing oxygen, may be made substitutes for nitre in the manufacture of gunpowder.

Paris, Dec. 10, 1813.